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PATENT SPECIFICATION

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(72) Inventor LOUIS J. BACCEI



(54) CURABLE POLY(ALKYLENE)ETHER POLYOL-BASED RESINS HAVING IMPROVED PROPERTIES

(71) We, LOCTITE CORPORATION, a corporation organised under the laws of the State of Connecticut, United States of America, of 705 North Mountain Road, Newington, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to poly(alkylene)-ether polyol-based resins, curable by peroxy initiation, and having improved impact, and cure-through-volume properties as well as good overall properties. More specifically, it relates to resins which may be viewed as a reaction product of poly(alkylene)ether polyols, preferably diols, with, e.g., methacrylate-capped aromatic diisocyanates.

It is known that curable anaerobic resins having desirable properties may be prepared as the reaction product of an organic polyisocyanate and an acrylate ester having an active hydrogen in the non-acrylate portion of the ester. Such resins are disclosed in U.S. Patent 3,425,988. This patent relates specifically to monofunctional, acrylate-terminated material which is reacted with an organic polyisocyanate in such proportions as to convert all of the isocyanate groups to urethane or ureide groups. The acrylate esters are preferably the acrylates and methacrylates containing hydroxy or amino functional groups on the non-acrylate portions thereof.

It is also known that poly(alkylene)ether glycols may be reacted with organic isocyanates to form urethane prepolymers which are subsequently cured by reaction with an active hydrogen molecule, e.g., with alcohols, amines, water, or other agents. Such systems are two-part systems, that is, the alcohol or amine must be kept separate from the prepolymer until the time of actual use since

the mixed system has very limited pot life. As would be expected, the mixing of these viscous liquids leads to problems of non-homogeneity and therefore imperfect cure, as well as causing substantial inconvenience. Similar urethane coatings curable through the action of moisture are also known, but have the defect that cure begins as soon as the coating is spread, thereby interfering with control of the coating operation and causing inconvenience.

Now, however, there is provided a polymerisable composition based on prepolymers which are derived from the reaction between poly(alkylene)ether polyols, preferably glycols, and organic polyisocyanates, preferably diisocyanates, which can be prepared as a one-part system having long pot life and more controllable cure characteristics. The prepolymers of this invention are also characterised by being acrylate, or methacrylate, terminated. These prepolymers are curable by free radical generating initiators, e.g., peroxy compounds or ultraviolet-sensitive compounds. When formulated with hydroperoxides, they acquire anaerobic curing characteristics. The compositions of this invention have broad utility as adhesives, sealants and coatings and generally provide, among other benefits, improved physical properties such as excellent tensile and impact strengths, good flexibility even at low temperatures, and excellent ability to cure through quite large gaps, e.g., 40—50 mils or more.

The present invention provides a curable adhesive and sealant composition comprising:

- I. a polymerisable product corresponding in structure to a reaction product of:
 - (a) a poly(alkylene)ether polyol (preferably glycol) with
 - (b) a molar excess of a reaction product of: at least a molar equivalent of an

aromatic or cycloaliphatic polyisocyanate with an aromatic or cycloaliphatic polyol or polyamine,

- the product f (a) and (b) subsequently being reacted with at least a molar equivalent of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate; and

II. a free radical initiator.

- There is also provided a process for preparing the monomer of Part 1, above, comprising:

I. reacting:

- (a) a poly(alkylene)ether polyol with (b) a molar excess of a reaction product of: at least a molar equivalent of an aromatic or cycloaliphatic polyisocyanate with an aromatic or cycloaliphatic polyol or polyamine,

- II. the product of (a) and (b) subsequently being reacted with at least a molar equivalent of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate.

- In addition, there is provided a process for sealing or adhering surfaces which comprises: (a) applying to at least one of the said surfaces an adhesive and sealant composition as defined above; and (B) placing the said surfaces in an abutting relationship until the composition has cured.

- The monomer used according to the present invention may be viewed as a one-component polymerisable block copolymer (prepolymer) having well-defined rigid and flexible segments. This is achieved by the chemical linking of two precursor "prepolymers" which are subsequently "capped" with acrylate, or methacrylate, functionality. Accordingly, in a preferred embodiment, a "flexible" polymeric alkylene ether diol segment of relatively low molecular weight is reacted with a molar excess of a "rigid" diisocyanate such as toluene diisocyanate or methylene diisocyanate (4,4'-diisocyanato diphenylmethane), thereby forming urethane linkages. Before reacting with the poly(alkylene)ether diol, the diisocyanate is reacted in excess with another rigid moiety which is an aromatic or cycloaliphatic polyol or polyamine containing at least two active hydrogen atoms, thereby capping the other rigid moiety with —NCO groups. By the term "rigid" segment is meant a segment or segments containing aromatic, or cycloaliphatic rings. If multiple segments are involved, they should be joined by either fusing of the rings or by a minimum of carbon atoms (e.g., 1 or 2 if linear, 1 to 8 if branched) such that there is little or no flexing of the segments. By the term "flexible" segment is meant a

segment comprising primarily linear aliphatic ether moieties. Pendent functional groups, including aromatic, heterocyclic and cycloaliphatic, among others, as well as branching, may also be incorporated, provided that there is no substantial interference with the necessary flexible nature of the linear portion nor degradation of the cured resin properties disclosed herein.

Illustrative of the polyisocyanates employed in the preparation of the new monomers are, among others, phenylene diisocyanate, toluene diisocyanate, 4,4'-diphenyl diisocyanate, 4,4'-diphenyl methane diisocyanate, dianisidine diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenyl ether diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane, cyclohexylene diisocyanate, tetrachlorophenylene diisocyanate, 2,6-diethyl-p-phenylenediisocyanate, and 3,5-diethyl-4,4'-diisocyanatodiphenylmethane. Still other polyisocyanates that may be used are the higher molecular weight rigid polyisocyanates obtained by reacting polyamines containing terminal, primary and secondary amine groups or polyhydric alcohols, for example, the cycloalkane, cycloalkene, and aromatic polyols such as bisphenol-A, with an excess of any of the above-described isocyanates. These higher molecular weight urethane or ureide polyisocyanates may be represented by the formula:



wherein R^1 is cycloalkylene, cycloalkenylene, arylene, aralkylene or alkarylene radical of from 2 to 20 carbon atoms, either substituted or unsubstituted; X is —O— or



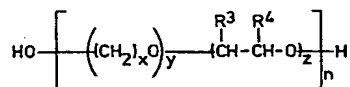
wherein R^2 is a hydrogen atom or a lower alkyl radical of 1 to 7 carbon atoms; B is a polyvalent cycloalkyl, cycloalkenyl, aryl, aralkyl, alkaryl or radical, either substituted or unsubstituted; and n is an integer from 2 to 6.

As indicated above, the diisocyanate is reacted with another rigid segment comprising an aromatic, or cycloaliphatic polyol or polyamine containing at least two active hydrogen atoms, preferably diamines and more preferably diols. Suitable compounds are 2,2-(4,4'-dihydroxydiphenyl)-propane (i.e., bisphenol-A), 4,4'-iso-propylidenedicyclohexanol (i.e., hydrogenated bisphenol-A), ethoxylated bisphenol-A, propoxylated bisphenol-A, 2,2-(4,4'-dihydroxydiphenyl)-butane, 3,3-(4,4'-dihydroxydiphenyl)-pentane, α,α' -(4,4'-dihydroxydiphenyl)-

5 *p* - diisopropylbenzene, 1,3 - cyclohexane diol, 1,4-cyclohexane diol, 1,4-cyclohexanedi-
methanol, bicyclic and tricyclic diols such as
4,8 - bis - (hydroxymethyl) - tricyclo-
10 [5.2.1.0^{2,6}] decane, 2,2,4,4 - tetramethyl-
1,3-cyclobutanediol, hydroquinone, resorcinol,
2,2 - (4,4' - dihydroxydiphenyl) - sulphone,
and 4,4'-oxydiphenol, among others, as well
as halogenated derivatives of the above, such
15 as tetrabrominated ethoxylated bisphenol-A.
These ring compounds may also be substituted
with either reactive groups or unreactive
groups such as alkyl groups containing 1 to 4
carbon atoms. This reaction may be carried
20 out at temperatures from room temperature
to 180° C, preferably 40 to 120° C, depending
upon the specific reactants selected. At the
lower temperatures, use of standard catalysts
may be desirable. Unreactive diluents may be
25 used, if desired.

The polyisocyanate thus formed is reacted
with a polymeric alkylene ether polyol having
at each end of the chain a functional group
containing a reactive hydrogen atom in a
hydroxyl group.

25 The poly(alkylene)ether or copoly-
(alkylene)ether compounds of this invention
preferably conform to the formula



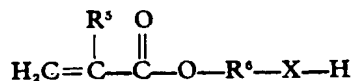
30 wherein *x* is an integer from 1 to 8, *y* is 0
or an integer from 1 to 20, *z* is 0 or an
integer from 1 to 10, and *n* is an integer of
1 to 100, with the proviso that *y* and *z*
can not simultaneously equal 0. Preferably, *x*
35 is 2 to 6, *y* is 1 to 5, *z* is 0 to 2, and *n* is 3
to 60. More preferably, *x* is 4 to 6, *y* is 1 or
2, *z* is 0 or 1, and *n* is 5 to 40. R³ and R⁴
may each be a hydrogen atom, a lower alkyl
radical containing 1 to 3 carbon atoms, a
40 cycloaliphatic, cycloalkenyl or aromatic radical
comprising up to 8 carbon atoms or a hetero-
cyclic radical comprising up to 8 carbon/
hetero atoms. It is also highly desirable that
the glycol be linear in order to provide a
45 high degree of flexibility in the segment.
Suitable linear polyols would include poly-
(tetramethylene)ether glycol and poly-
(ethylene)ether glycol, among others. Repre-
sentative branched polyols include poly(1,2-
50 propylene) ether glycol and poly(1,2- or 1,3-
butylene)ether glycol. Preparation and proper-
ties of polyols of these types are discussed in
the literature, e.g., Saunders, J. H., and
55 Frisch, K. C., "Polyurethanes - Chemistry
and Technology," Interscience, New York,
New York, (1963).

The flexible poly(alkylene)ether having
functional groups containing an active
hydrogen is reacted with the polyisocyanate in
60 such proportion that the polyisocyanate is

present in molar excess as to the concentration
of the active hydrogen-containing groups. In
this way a product is assured which has an
—NCO group at each end of the poly-
(alkylene)ether segment. The molar excess of
polyisocyanate may vary from 0.05 to 6.

This reaction may be carried out at tem-
peratures from room temperature to 150° C,
preferably from 40° C to 120° C. After addi-
tion of the flexible diol, 0.1 to 30 hours are
required for completion at the preferred tem-
perature range. The reaction may also be
catalysed, if desired, and unreactive diluents
may be used for viscosity control.

The product of the above reaction is reacted
75 with at least a molar equivalence, preferably
a molar excess, based on —NCO group con-
tent, of an acrylate or methacrylate ester con-
taining a hydroxy or amine group on the
nonacrylate portion thereof. This results in
an adhesive/sealant monomer, or more
accurately, prepolymer, capped at both ends
with acrylate or methacrylate functionality.
Esters suitable for use in this invention corres-
80 pond to the formula



wherein X is as previously defined, R⁵ is
hydrogen or a methyl or ethyl radical; and
R⁶ is a divalent lower alkylene radical of
1—8 carbon atoms, phenylene or naphthylene
90 radical.

The suitable hydroxy- or amine-containing
materials are exemplified by, but not limited
to, such materials as hydroxyethyl acrylate,
hydroxyethyl methacrylate, aminoethyl, meth-
95 acrylate, 3-hydroxypropyl methacrylate,
aminopropyl methacrylate, hydroxyhexyl
acrylate, t-butylaminoethyl methacrylate and
hydroxyoctyl methacrylate.

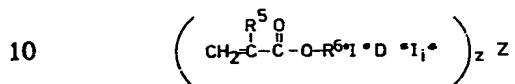
The reaction may be accomplished in the
presence or absence of diluents. Preferably,
diluents which include the hydrocarbons, such
as aliphatic, cycloaliphatic and aromatic
hydrocarbons, for example, benzene, toluene,
cyclohexane, hexane and heptane are em-
100 ployed, but other diluents, such as methyl
isobutyl ketone, diamyl ketone, methyl meth-
acrylate, isobutyl methacrylate, lauryl meth-
acrylate, isobornyl methacrylate, and cyclo-
hexyl methacrylate can also be beneficially
used, if desired, especially where complete
compatibility with the sealant system is desired.
Mixtures of diluents may also be used.

The temperature employed in the reaction
may also vary over a wide range. Where the
components are combined in approximately
chemical equivalent amounts, useful tempera-
105 tures may vary from room temperature or
below, e.g., 10° C to 15° C, up to and includ-
ing temperatures of 100° C to 180° C. Where
reacting the simpler isocyanate adducts, the

components are preferably combined at or near room temperature, such as temperatures from 20° C to 30° C. At the lower reaction temperatures, the use of a catalyst is preferred.

5 When reacting the higher molecular weight isocyanate adducts, higher temperatures are preferred, e.g., 40° C to 150° C.

The fully-prepared monomeric prepolymers of this invention correspond to the formula



wherein R⁵ and R⁶ are each as previously defined; I is a polyisocyanate radical; D is an aromatic, or cycloaliphatic polyol or polyamine radical, preferably a diol, and more preferably a diol of a cycloaliphatic compound; Z is a polymeric or copolymeric alkylene ether polyol radical as already described; z is an integer corresponding to the valency of Z; and i is equal to one less than the number of reactive hydrogen atoms of D. As used herein, an asterisk (*) indicates a urethane (—NH—COO—) or ureide (—NH—CO—NH—) bond.

The prepolymer described above cures to a hard, tough resin via a free-radical mechanism using any of a wide variety of known peroxy initiators. Illustrative of such initiators are the diacyl peroxides such as benzoyl peroxide; dialkyl peroxides such as di-tert.-butyl peroxide; ketone peroxides such as methylethyl ketone peroxide; and peresters which readily hydrolyse, e.g., tert.-butyl peracetate, tert.-butyl perbenzoate and di-tert.-butyl diperphthalate. A particularly useful class of peroxy initiators are the organic hydroperoxides such as cumene hydroperoxide, methylethyl ketone hydroperoxide and tert.-butyl hydroperoxide. Of these, cumene hydroperoxide is especially preferred. The initiators should be used at a concentration of 0.01 percent to 10 percent by weight of the total formulation, preferably 0.1 percent to 5 percent by weight. Another useful class of initiators comprises carbonyl-containing ultraviolet-activated free-radical generators, such as acetophenone, benzophenone, and the benzoin ethers. Suitable UV initiators are disclosed in UK Specification No. 1,430,422. Initiator mixtures may also be used.

It will be understood that the curable composition of this invention can also be formulated as a two-part composition. In such a case, the initiator or one of a combination of initiators can comprise a second part which is combined with the first, monomeric, part at the point of use. Thus, the monomer can be applied to one surface to be joined, the initiator can be applied to a second surface, and the two surfaces then joined. Similarly, an accelerator, such as mentioned below, can

be applied separately as a second part to one of the surfaces to be joined, e.g., as a "primer".

It may be desirable to accelerate the cure polymerisation by application of moderate amounts of heat, e.g., 50° C to 150° C. At temperatures above 125° C, cure will typically be complete within 10 minutes or less.

The prepolymers of this invention can be formulated into room temperature-curing anaerobic adhesives and sealants. Formulations of this type are well described in the art, e.g., United States Patent 3,043,820, among others, using the hydroperoxide class of initiators. Such anaerobic formulations may also advantageously include polymerisation accelerators such as organic imides (e.g., benzoic sulphimide) and primary, secondary or tertiary amines, and inhibitors or stabilisers of the quinone or hydroquinone families. The accelerators are generally employed in concentrations of less than 10 percent by weight, and the inhibitors in concentrations of 10 to 1,000 parts per million. When prepared as anaerobic formulations, the compositions of this invention have the advantage of long-term stability and the ability to cure at room temperature upon exclusion of oxygen, as between the mating threads of a nut and bolt or the juxtaposed surfaces of a bearing and shaft. The anaerobic cure speed can be enhanced by application of moderate heat, e.g., up to 150° C.

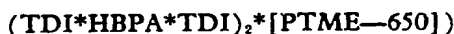
The adhesive and sealant formulations of this invention may be prepared, if desired, with reactive diluents, and mixtures thereof, which are capable of copolymerising with the prepolymers. Typical of such diluents are the hydroxyalkyl acrylates and diacrylates such as hydroxyethyl acrylate, hydroxypropyl acrylate, and the corresponding methacrylate compounds, including cyclohexyl methacrylate, methyl methacrylate, isobornyl methacrylate, lauryl methacrylate, triethylene glycol dimethacrylate, isobutyl methacrylate and tetrahydrofurfuryl methacrylate. Other unsaturated reactive diluents, such as styrene and acrylonitrile, can also be used. When used, the concentration of such diluents should be less than 60 percent by weight, and preferably 40 to 10 percent.

One of the significant advantages of the prepolymers of this invention is their exceptional ability to cure through large gaps, e.g., up to 85 mils. This behaviour may be enhanced by application of moderate heat. Preferably, however, it is enhanced by use of any of the primers known for anaerobic systems, such as those disclosed in United States Patent 3,625,930, and particularly those of the thiourea type disclosed in United States Patent No. 3,970,505. Such primers are advantageously applied as a spray from dilute solvent solution to either or both surfaces to be joined.

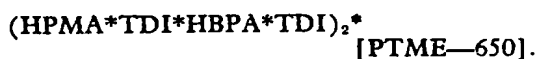
The following examples provide specific illustrations of various aspects of the present invention and are in no way limitations on it.

EXAMPLE 1.

5 A nitrogen-swept 4-necked resin kettle equipped with a stainless steel stirrer, nitrogen inlet tube, thermometer, condenser and entrance port, was charged with 69.6 grams of toluene diisocyanate (TDI) (80% 2,4-/ 10 20% 2,6—). The TDI was heated to 95 to 100° C. Thirty-six grams of hydrogenated bisphenol-A (HBPA) was added slowly in 2 hours. Fifteen minutes after the HBPA addition was completed, a solution of 60 grams triethyleneglycol dimethacrylate (TRIEGMA) 15 and 300 ppm of a quinone stabiliser was added slowly over a 10 minute period. Fifteen minutes later, addition of 12.0 grams HBPA in 4 to 6 portions was performed. HBPA 20 minutes after all the HBPA was in (total, 48.0 grams), the bath temperature was lowered such that the reaction temperature was at 60 to 65° C. The reaction mixture consisted of toluene diisocyanate capped-HBPA prepolymer(s) (abbreviated 25 TDI*HBPA*TDI) dissolved in TRIEGMA. To the reaction solution was added 62.1 grams of a Polymeg 650 glycol over a 1½ hour period. The reaction solution was maintained at 60 to 65° C and heating and stirring were continued for approximately one hour after completion of the glycol addition. The reaction mixture consisted of 30 TDI*HBPA*TDI capped Polymeg 650 (pre-polymer(s) (abbreviated 35



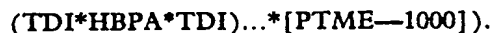
dissolved in TRIEGMA. A solution of 43.3 grams of 96% hydroxypropyl methacrylate (HPMA), 1.8 grams TRIEGMA, and 100 40 ppm of a quinone stabiliser was added and the reaction solution was maintained at 65 to 70° C for approximately 1½ hours. The resultant solution contained approximately 72% concentration of urethane dimethacrylate structures corresponding to the general formula 45



EXAMPLE 2.

To a nitrogen swept resin kettle, equipped as described in Example 1, was charged 69.6 50 grams of TDI. The TDI was heated to approximately 95° C. Thirty-six grams of HBPA was added slowly in 1½ hours. Fifteen minutes after the HBPA additions were completed, a preheated (about 50° C) solution of 45.0 grams of TRIEGMA and 150 ppm 55 of a quinone stabiliser was added over a 10-minute period. When the reaction temperature reached 95° C, addition of 12.0 grams of HBPA in 4 to 6 portions was performed.

Fifteen minutes after the completion of HBPA 60 additions, the bath temperature was lowered such that the reaction temperature dropped to 60 to 65° C. To the reaction solution was added 96.2 grams of a polytetramethylene 65 ether glycol (Polymeg 1000) in approximately 2 hours. Heating and stirring were continued at 64 to 69° C. A sample for NCO analysis was removed one-half hour after completion of the glycol addition. A titer of 3.35% NCO 70 (vs 3.22% theoretical) was obtained for the reaction solution. Apparently, the desired TDI*HBPA*TDI-capped ether prepolymer(s) was formed (abbreviated

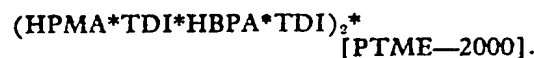


A diluent solution of 36.4 grams of TRIEGMA 75 and 150 ppm of a quinone stabiliser was added to maintain a fluid reaction medium. Finally, 48.0 grams of 96% hydroxypropyl methacrylate was added to cap the prepolymer ends with methacrylate functionality. The 80 resultant solution contained approximately 70% concentration of urethane dimethacrylate structures corresponding to the general formula



EXAMPLE 3.

To a nitrogen swept resin kettle, equipped as described in Example 1, was charged 34.8 grams TDI. The TDI was heated to 100° C. 90 Eighteen grams of HBPA was added slowly in 1½ hours. Fifteen minutes after the HBPA addition was completed, a preheated (about 50° C) solution of 35.0 grams of TRIEGMA and 150 ppm of a quinone stabiliser was added over a 5-minute period. Fifteen minutes 95 later, addition of 6.0 grams of HBPA in 3 to 5 portions was performed. Upon completion of the HBPA additions, the bath temperature was lowered such that the reaction temperature settled to 60 to 65° C. To the reaction 100 solution was added 98.2 grams of a 2000 molecular weight polytetramethylene ether glycol (Polymeg 2000) within 2½ hours. Heating and stirring were continued for an additional hour at 60 to 70° C. A diluent 105 solution of 15.2 grams of TRIEGMA and 150 ppm of a quinone stabiliser was added to maintain a fluid reaction medium. Hydroxypropyl methacrylate (96%, 27.4 grams) was added over a 5-minute period and heating 110 was continued for an additional hour at 60 to 65° C. The resultant solution contained approximately 72% concentration of urethane dimethacrylate structures corresponding to the general formula 115



EXAMPLE 4.

To a nitrogen swept resin kettle, equipped as described in Example 1, was charged 52.4 grams of liquid, hydrogenated MDI (H_{12} -MDI, Hylene W, E. I. du Pont de Nemours and Company, Wilmington, Delaware). The H_{12} -MDI was heated to approximately 100° C. To the diisocyanate was added 10.8 grams of (CHDM) cyclohexanedimethanol over a 20-minute period. This was followed by the addition of a diluent solution of 35.0 grams of TRIEGMA and 150 ppm of a quinone stabiliser over a 10-minute period. When the temperature reached 100° C, 3.6 grams of cyclohexanedimethanol was added slowly. Approximately one-half hour later, a sample was removed for NCO analysis. Titration revealed a titer of 8.40% NCO versus a theoretical (including solvent) titer of 8.10%. Apparently, the desired



prepolymer was achieved. The bath temperature was lowered such that the temperature of the solution settled to 60 to 70° C. To the reaction solution was added 98.3 grams of a 2000 molecular weight polytetramethylene ether glycol within 1 to 2 hours. Approximately one hour later, another diluent solution was added (29.1 grams of TRIEGMA and 150 ppm stabiliser). Another sample was withdrawn for NCO analysis. Titration revealed a titer of 3.55% NCO vs a theoretical of 3.62% NCO. Again, the desired prepolymer(s) was apparently formed:



Hydroxypropyl methacrylate (96%, 44.4 grams) was added over a 10-minute period. Heating was continued at 60 to 65° C. The resultant solution contained approximately 70% concentration of urethane dimethacrylate structures corresponding to the general formula



EXAMPLE 5.

This example illustrates a typical anaerobic adhesive formulation using any of the prepolymers, or mixtures thereof, described above. With good stirring, add 4.6 grams of hydroxypropyl methacrylate to 79 grams of the prepolymer resin product solution (70 to 75 percent solids). A slurry of 0.38 gram saccharine in 3.8 grams of triethyleneglycol dimethacrylate is then stirred in. Subsequently, 5.6 grams of acrylic acid (adhesion enhancer) and 2.8 grams of cumene hydroperoxide (CHP) are added and stirring is continued for about 1 hour. Minor amounts of stabilisers, accelerators, thickeners and plasticisers, may be added, as desired, as is known in the art.

EXAMPLE 6.

Anaerobic adhesive formulation were prepared similar to Example 5 using the prepolymers of Example 1-4.

TABLE I

Prepolymer	General Structure
A	$(HPMA*TDI*HBPA*TDI)_2*[PTME-650]$
B	$(HPMA*TDI*HBPA*TDI)_2*[PTME-1000]$
C	$(HPMA*TDI*HBPA*TDI)_2*[PTME-2000]$
D	$(HPMA*H_{12}-MDI*CHDM*H_{12}-MDI)_2*[PTME-2000]$

The typical strength properties for these adhesive formulations are reported in Table II, below. Tensile strength measurements were performed according to ASTM D-2095-72. Simply described, this test involves adhering together two steel rods by butt joining their respective ends. The opposite rod ends are then pulled with a measuring device such as an Instron Tester ("Instron" is a Registered Trade Mark), and the tensile strength of the bond is measured. The tensile lap shear test was performed according to

ASTM-D-1002-65.

This test involves adhering together overlapping surfaces of two steel test strips. The ends of the so-assembled specimens are pulled with a measuring device such as an Instron Tester, and the tensile shear strength of the bond is measured. Compressive shear, tested according to military specification

MIL-R-46082A(MR),

measures the ability of an adhesive to retain a sleeve or bearing on a shaft. The test involves adhering a cylindrical "pin" within

35

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45

50

55

60

80

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- the bore of a mating collar. The force required to press the pin from the collar is then measured on an Instron Tester or equivalent. Impact strength was tested according to ASTM—D—950—72. This test involves a steel block mated to another steel block with adhesive and then struck by a swinging pendulum device, such as a Baldwin Impact Tester. The impact force required to separate the blocks is measured. Heat (200°F) was used, for convenience, to accelerate cure in all tests; for one hour in the tensile and compressive shear tests, and for 1½ hours in the impact test.

TABLE II

Prepolymer- Adhesive Formulation	Tensile, psi	Tensile Lap Shear psi (Steel laps, sand blasted)	Compressive Shear, psi	Impact Strength, ft. lbs./ sq. in.
A	7390	4100	5345	13.2
B	9215	4150	4220	13.0
C	4650	3365	3325	10.2

EXAMPLE 7.

- Another significant merit of the present prepolymers when formulated as adhesive is their ability to cure through relatively large gaps, e.g., 20 mils or more, to form structurally strong bonds with very high impact strengths. Table III illustrates typical tensile shears (room temperature cured on sand-blasted steel surfaces primed with a tetramethyl thiourea activator known to the art) and impact strengths (cured either by the above activator at room temperature or heat cured for one and one-half hour at 200° F).

TABLE III

Impact Strength ft.lbs./sq. in.

Prepolymer	Tensile Shear, psi, 20-mil gap	20-mil gap (primer)	20-mil gap (heat cured)	55-mil gap (heat)
B	2405	13.3	12.1	
C	1195	15.7	12.5	11.2
D		9.7	10.1	3.6

EXAMPLE 8.

- A further distinct advantage of the present prepolymers is their excellent strengths under cryogenic conditions. This is illustrated in Table IV, which presents the exceptionally high impact strength, even at large gaps, found for the adhesive formulations, as in Example 6, of representative materials at low test temperatures. A gap of 0 mils simply means that there is virtually no gap between the adhesively joined steel blocks. Heat (200° F, 1½ hours) was used, for convenience, to accelerate cure in all samples. The blocks were then cooled to the appropriate temperature and promptly tested; otherwise, the impact test procedure was as previously described.

TABLE IV

Impact Strength, in ft.lbs./sq.in.

Prepolymer	Room Temperature	0°C	-40°C	-80°C
B 0 mils	13.4	25.8		23.7
20 mils	12.1	11.5		2.7
C 0 mils	10.2	13.3	18.5	18.7
20 mils	14.6	15.1	11.6	8.0

EXAMPLE 9.

An adhesive formulation was prepared using prepolymer B (Table I) according to the procedure of Example 5, except that 3 to 5% (based in total formulation weight) of benzoyl peroxide was substituted for the CHP and saccharine. A 2 to 5 mil thick film of the formulation was spread on a steel plate and placed in a 200° F oven for 1½ hours, then cooled to room temperature. The formulation cured to a dry, durable film.

A tensile lap shear test (as previously described) was performed. A heat cure was applied (200° F, 1 hour), resulting in a bond strength of 3400 psi.

WHAT WE CLAIM IS:—

1. A curable adhesive and sealant composition comprising:

- I. a polymerisable product corresponding in structure to a reaction product of:
- a poly(alkylene)ether polyol with
 - a molar excess of a reaction product of: at least a molar equivalent of an aromatic or cycloaliphatic polyisocyanate with an aromatic or cycloaliphatic polyol or polyamine,

the product of (a) and (b) subsequently being reacted with at least a molar equivalent of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate; and

II a free radical initiator.

2. A composition as claimed in claim 1, wherein the poly(alkylene)ether polyol is linear.

3. A composition as claimed in claim 2, wherein the poly(alkylene)ether polyol is poly(tetramethylene)ether glycol.

4. A composition as claimed in any of claims 1 to 3, wherein the polyisocyanate is toluene diisocyanate.

5. A composition as claimed in any of claims 1 to 3, wherein the polyisocyanate is 4,4'-diisocyanato diphenylmethane.

6. A composition as claimed in any of claims 1 to 3, wherein the reaction product (b) is an NCO-terminated product of hydrogenated bisphenol-A and toluene diisocyanate.

7. A composition as claimed in any of Claims 1 to 6, wherein the hydroxyalkyl methacrylate is hydroxyethyl methacrylate.

8. A composition as claimed in any of Claims 1 to 6, wherein the hydroxyalkyl methacrylate is hydroxypropyl methacrylate.

9. A composition as claimed in any of Claims 1 to 8, which additionally contains an organic solvent.

10. A composition as claimed in Claim 9, wherein the solvent is a co-reactive solvent.

11. A composition as claimed in Claim 10, wherein the solvent is isobornyl methacrylate.

12. A composition as claimed in Claim 10, wherein the solvent is cyclohexyl methacrylate.

13. A composition as claimed in Claim 10, wherein the solvent is lauryl methacrylate.

14. A composition as claimed in Claim 10, wherein the solvent is hydroxypropyl methacrylate.

15. A composition as claimed in Claim 10, wherein the solvent is tetrahydrofurfuryl methacrylate.

16. A composition as claimed in any of Claims 1 to 15, wherein the initiator is an ultraviolet-activated initiator.

17. A composition as claimed in any of Claims 1 to 15, wherein the initiator is a peroxy initiator and the composition is anaerobically curing.

18. A composition as claimed in Claim 17, wherein the peroxy initiator is a hydroperoxide.

19. A composition as claimed in Claim 18, wherein the hydroperoxide is cumene hydroperoxide.

20. A composition as claimed in any of Claims 17 to 19, which additionally contains a polymerisation accelerator.

21. A composition as claimed in claim 20, wherein the accelerator is an imide or an amine.

22. A curable adhesive and sealant composition substantially as described with particular reference to any of Examples 5 to 9.

23. A process for preparing an adhesive and sealant monomer comprising:

I. reacting:

- a poly(alkylene)ether polyol with
- a molar excess of a reaction product of: at least a molar equivalent of an aromatic or cycloaliphatic polyisocyanate with an aromatic or cycloaliphatic polyol or polyamine,

II. the product of (a) and (b) subsequently being reacted with at least a molar equivalent of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate.

24. A process for preparing an adhesive and sealant monomer substantially as described with particular reference to any of Examples 1 to 4.

25. A process for adhering surfaces which comprises:

- applying to at least one of the said surfaces an adhesive and sealant composition as claimed in any of claims 1 to 22; and
- placing the said surfaces in an abutting relationship until the composition has cured.

26. A process for sealing a surface which comprises:

- 5 (A) applying to the surface an adhesive and sealant composition as claimed in any of claims 1 to 22; and
(B) allowing the composition to cure.

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